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Detection of Molecular Infrared Spectra

The effect of adsorbed molecules on the total energy distribution (TED) of field emitted electrons has been investigated. The expectation was that tunneling electrons would interact electronically with bonding electrons of the adsorbate so as to perturb the TED in such a way as to give information regarding the binding forces between the adsorbed atom and the surface. These theoretical expectations have been realized to some degree in practice and thus have provided insight as to bonding modes of certain adsorbate-substrate systems. On the basis of work by others using internal solid state field emission devices, another possible aspect of this application was deduced: namely, the detection of molecular infrared spectra of adsorbed molecules from TED measurements of field emitted electrons. Basically, the idea is as follows:

A tunneling electron can give up a quantum of energy $h\nu$ to excite various vibrational, rotational, and possibly electron modes of the adsorbed molecule. These electrons, when energy-analyzed by a retarding potential analyzer, will show up on the collector at a tip-to-collector bias potential $V_b = -O_c - h\nu$, where O_c is the collector work function. The derivative of the collector current dI_c/dV_b versus V_b will show a peak at $V_b = O_c - h\nu$ and thus exhibit the spectra of the various modes excited by the tunneling electrons.

In recent experiments these results were confirmed with various organic compounds on a tungsten surface. These findings provide a new and significant tool for obtaining spectra of adsorbed molecules. The range of equivalent wavelength covered has been shown to extend over the near and far infrared spectrum (1.0

to 30 microns). The sensitivity is such that a monolayer of material is sufficient, and the resolution is theoretically limited by the thermal electrons above the barrier, which can be reduced to less than 10 mV by cooling the emitter to 4°K. Molecules can be examined after heating the tip to various temperatures in order to study the decomposition modes for catalytic-type investigations.

The ease of sample introduction (evaporation and condensation onto the tip) and the large spectral range of this device provides decided advantages over the internal field emission method described by J. Lambe and R. Jaklevic, Phys. Rev. **165**, 821 (1968). This tool has significant interest for the surface chemist in that it provides a way to obtain surface infrared spectra of adsorbed molecules and decomposition products. Because of this spectral range, it has prospects as a general analytical spectrometer to the organic and inorganic spectroscopist.

Note:

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